

Dissolution of Co from Electrodeposited Cu/Co and Cu/Ni-Co Sandwiches

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Introduction: The discovery of giant magnetoresistance (GMR) in electrodeposited multilayered thin films has greatly stimulated research on the fabrication of super lattices. Extensive work has been carried out to improve the GMR of electrodeposited metal multilayers such as Cu/Co, Cu/Ni, Ag/Co. However, most investigators have looked for different combinations of metals, better substrates and appropriate structures, etc, to improve GMR properties. Relatively less attention has been paid to determine the role electrochemical parameters such as electrode potential, electrolyte composition and pH, etc on the nucleation and growth of multilayers, aspects which may be crucial to the properties of such layers.

One of the major problems of multilayer electrodeposition process is that the less noble component, usually the magnetic one, dissolves during the deposition of nobler one^{1,2}. It has been found that Ni dissolution during electrodeposition of Cu/Ni multilayers is stifled quickly by the formation of a 10-50 Å Cu layer³. However, the dissolution mechanism of Co from Cu/Co multilayer is not well understood.

Experimental: Solutions containing only 0.0125 M CuSO₄·5H₂O or 0.25 M CoSO₄·7H₂O or both were used. In all electrolytes 0.256 M Na₃Cit was added. The pH of the electrolytes was adjusted to 1.75 using H₂SO₄. A platinum coated titanium mesh was used as counter electrode. A gold RDE was fixed at 1200 rpm.

Cyclic voltammetry was carried out using Model 366A bi-potentiostat. All potentials were measured against a saturated calomel electrode placed approximately 1 cm away from the RDE. The potential was swept at the rate of 10 mV/s.

Results and Discussion: Simple cyclic voltammograms of identical electrolytes containing Cu and Co are shown in Fig. 1a & 1b respectively. As the reduction potential of Cu is much lower than that of Co, only Cu was deposited on the gold surface first, then deposition of Co was occurred on the Cu layer. When the scan direction reversed from -2000 mV, Co deposition stopped at around -1100 mV but Cu continued to deposit. Thus a sandwich of Cu/Co/Cu multilayer was made, where the outer Cu layer was ca. 4882 Å thick. However, the sweep rate was reduced to 2 mV/s when the potential approached to the dissolution point (-300 mV) of the multilayer.

The figures show that Cu dissolution occurs at around 0 mV and Co dissolution occurs at approximately -300 mV in citrate bath of pH 1.75. The polarization curve of cobalt also shows that all deposited cobalt has dissolved before the potential reaches at 0 mV. Fig. 1c shows the cyclic

voltammogram of the Cu/Co system. In this case the sweep rate is reduced from 10 mV/s to 2 mV/s when the potential approached the dissolution point of Co. As a

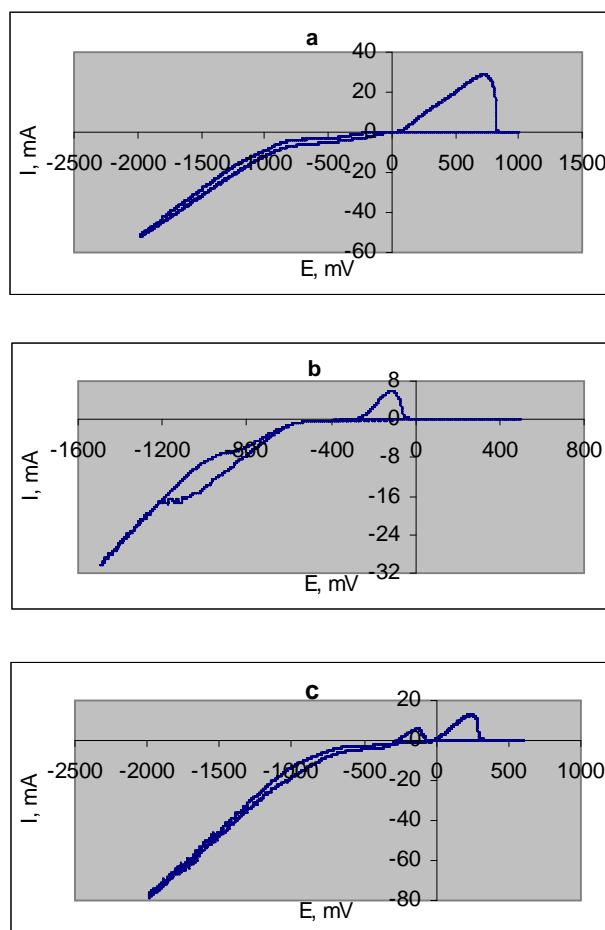


Fig. 1: Cyclic voltammograms for (a) Cu, (b) Co and (c) Cu/Co systems; pH, 1.75; rotation, 1200 rpm.

result, all Co dissolved in negative potential regime and the anodic current dropped to zero. Then Cu started to dissolve at zero potential. This shows that Co dissolution occurs from the beneath of Cu layer. Voltammograms for Cu/Ni-Co deposition showed that Ni dissolution is stifled after the formation of thin copper layer on it during multilayer electrodeposition.

The difference in the behavior of the two systems is attributed to:

- (1) nucleation of copper is facile on nickel because the two metals alloy, thereby quickly covering the surface
- (2) nucleation of copper on cobalt is difficult because they are immiscible and
- (3) copper may form isolated islands and further discharge of copper occurs preferentially on these islands leaving cobalt uncovered and prone to electrodisolution.

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References: 1. S Roy, M Matlosz and D Landolt, *J. Electrochem. Soc.*, **141**, 1509 (1994).
2. S Roy, *Surf. Coat. Technol.*, **105**, 202 (1998).
3. P Bradley, S Roy and D Landolt, *J. Chem. Soc., Faraday Trans.*, **92**, 4015 (1996).